

CO-PROCESSING OF COAL AND RESID UNDER DELAYED COKING CONDITIONS

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Introduction

Delayed coking is a universal conversion process which utilizes long reaction times to produce gases, distillates and coke from relatively low value feedstocks such as vacuum resid [1,2]. It does not suffer from many of the inherent disadvantages associated with direct liquefaction, i.e. high pressure operation in hydrogen atmospheres, and hence is an attractive alternative to conventional coprocessing methods. In practice [1-3], the feed is rapidly heated to ca 500 °C in the coke drum. The vapor products (gases, naphtha and gas oil) are stripped off and sent to a fractionator tower whilst the coke remains in the drum, reacting to produce a high quality coke. The distillates can be subsequently catalytically upgraded to produce synthetic fuels. One further advantage is that the associated condensation reactions produce a highly aromatic coke enriched in S, N and metals relative to the feed. Typical product distributions from industrial coking operations are: 10-15% gas; 50-60% liquids; 30-35% coke [1-3].

Optimum coal/resid coprocessing conditions are governed by many factors including feed characteristics and reaction conditions [4-6]. Wallace and co-workers reported an improved interaction between coal and petroleum residua with resid Car values >40% [7]. Curtis and Hwang observed a decreased oil yield and increased asphaltene, preasphaltene and residue concentrations commensurate with addition of 30 wt% coal to residuum [8].

The work presented here represents a continuation of previous studies, primarily concerned with evaluation of retrogressive studies during coal/oil coprocessing [9,10]. Rather than focussing on the relative yields of soluble and insoluble product, this present work will incorporate qualitative analysis of the liquid products.

Experimental

Samples Three petroleum vacuum residua were used in the duration of this work. Elemental and NMR analyses are presented in Table 1. The residua were used as received. Six coal samples were utilized in this study from the Penn State Coal Sample Bank and Data Base. Analyses of the relevant samples are summarized in Table 2. Samples were ground to -60 mesh and dried under vacuum at 110 °C for 2 hours prior to use.

Coprocessing The reactions were carried out in vertical 25 ml microautoclave reactors with ca 8g feed (resid:coal ratio of 2:1 w/w) at 450 °C for 60 and 120 min. Tests were conducted under 3.5 MPa and atmospheric N₂ environments, respectively. The gaseous products vented and the liquid and solid products recovered and separated by sequential Soxhlet extraction into *n*-hexane solubles (oils), toluene solubles (asphaltenes) and THF solubles (preasphaltenes). The THF-insoluble residue was washed with acetone followed by *n*-pentane to remove any residual THF.

All recovered products were finally dried under vacuum at 110 °C for ca 10 hours. The conversion of coal into soluble products and gases was calculated on the basis of recovered THF-insoluble residue and reported on a dry, ash free (daf) basis. The concentration and composition of the liquid component was determined by GC/GC-MS to evaluate the contribution of the coal and resid to the overall reaction mechanism.

GC/GC-MS *n*-Hexane soluble products were analyzed by GC and GC-MS using a Hewlett Packard 5890 II GC coupled with an HP 5971 A mass spectrometer operating at electron impact mode (EI, 70 eV). The column was a DB-17 column; 30m x 0.25mm, coated with 50% phenyl 50% methylpolysiloxane with a film thickness of 0.25µm. A temperature program of 40 to 280 °C at heating rate of 4 °C/min and a final holding time of 15 min were used.

Results and Discussion

Figures 1 and 2 summarize the reaction conversions for the experiments conducted at 60 and 120 min, respectively, comparing the amount of THF-insolubles from coprocessing resid independently and in the presence of coal. Although the two sets of data were compiled under slightly different reaction conditions, they serve to illustrate that concentrations of THF-insoluble material are comparable for the two sets of feed.

At 450 °C, coking the coals and resid together for 60 min under 3.5 MPa N₂ was found to produce more solids than the sum expected from the independent reactions. Obviously, coal retrogressive reactions dominate at this higher temperature. However, it may also be that these resids coke more readily in the presence of coal, as suggested by the lower THF concentrations from similar reactions with a more aromatic resid [10].

There are many possible reaction mechanisms in coprocessing, as each of the feedstocks can lead to a variety of products. Therefore, it must be stressed that the separation of coprocessing products into insoluble and soluble material does not discriminate between the amount of insoluble matter originating from the independent reactions of the coal or residuum or, indeed, any resultant interactions. The overall negative conversions measured at 450 °C (Table 3) may be a result of the coking reactions of each feedstock independently or the product of interactions between the two components.

From Table 3, it can be seen that the presence of coal in the coking medium presents no significant deterioration in product distribution, with the bituminous coals displaying similar conversion data, especially asphaltene and preasphaltene concentrations. However, as anticipated there appears to be a rank effect on the enhancement of coke formation. This is in agreement with the preliminary results presented here. An important criterion in behavior in coprocessing systems is that the interactions leading to retrogressive reactions are influenced by the thermoplastic properties of the feedstock. Indeed, retrogressive reactions only arise when both the coal and the residuum are undergoing active thermal decomposition. The bituminous coal were therefore chosen, in part, due to their fluidity profiles. The existence of a fluid-like state enhances mixing with the resid and enables hydrogen transfer reactions. This is illustrated by the improved liquid product distribution in reactions of Pittsburgh #8, Upper Banner and Illinois #6 with VR1; all have maximum fluidity in the temperature range of 410-447 °C. Conversely, Wyodak coal, a low-rank subbituminous sample, demonstrates no plastic behavior, as reflected by the smaller THF-insoluble residue concentration; subbituminous coals offer restricted mobility and contact in comparison to their higher rank counterparts, resulting in limited surface interactions with the residuum components.

As cited earlier, product quality is a factor in determining the "success" of any experiment. Preliminary analysis of the n-hexane soluble fraction (oils) has shown significant differences in composition between samples from the latter reactions. A selected chromatogram is shown in Figure 3. VR1 oils are characterized by mainly small chain paraffins and 1-2 ring hydroaromatic structures. However, upon reaction in the presence of coal (irrespective of rank) heavier hydroaromatics were identified; in each case, selected 4 ring structures such as benzo(a)pyrene were observed.

Conclusions

Microautoclave reactions conducted with a range of coals and commercial residua demonstrated that at 450 °C and reaction times of 60 and 120 min, vacuum residua coke more readily in the presence of coals. Continued characterization of both the soluble and insoluble products by standard analyses such as HPLC, NMR, FTIR, optical microscopy, will determine the contribution of the coal and resid to the overall reaction mechanism. Finally, the solvating capacity of petroleum feedstocks has been reported to be enhanced by addition of an aromatic species, such as anthracene oil [11]. Further work will therefore include reactions with ternary systems, e.g. addition of decant oil to resid/coal mixtures.

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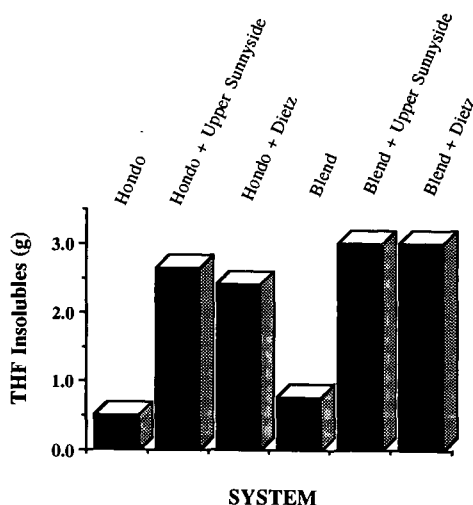
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Table 1. Properties of Petroleum Residua.

| Resid | Hydrogen Distribution | | | | Elemental Composition (%w/w) | | | | |
|-------|-----------------------|------------|-----------|------------|------------------------------|-------|------|------|------|
| | Har | H α | H β | H γ | C | H | N | S | H/C |
| VR1 | 6.44 | 12.58 | 62.88 | 18.11 | 85.9 | 10.82 | 0.43 | 1.53 | 1.51 |
| Hondo | 10.7 | 7.9 | 52.7 | 26.5 | 79.1 | 10.50 | 0.80 | 5.45 | 1.58 |
| Blend | 10.5 | 12.7 | 60.7 | 16.2 | 84.8 | 9.9 | 0.61 | 4.74 | 1.39 |

Table 2. Analysis of Project Coals.

| | | Coal | | | | | |
|--|--------------------|--------------------|-------|------------------|-----------------|----------------|--------|
| | | Upper Sunnyside | Dietz | Pittsburgh #8 | Upper Banner | Illinois #6 | Wyodak |
| | Rank | hvAb | subB | hvAb | hvAb | hvCb | subC |
| Proximate Analysis (wt%, as received) | Moisture | 3.38 | 23.66 | 2.40 | 2.44 | 13.20 | 28.42 |
| | Ash | 7.54 | 5.35 | 10.0 | 6.2 | 11.62 | 9.90 |
| | Volatile Matter | n/a | n/a | 35.16 | 33.46 | 35.44 | 32.38 |
| | Fixed Carbon | n/a | n/a | 52.44 | 57.89 | 39.74 | 29.30 |
| Ultimate Analysis (wt%, daf) | C | 82.0 | 76.0 | 83.3 | 86.6 | 76.3 | 74.4 |
| | H | 5.8 | 5.2 | 5.7 | 5.5 | 5.3 | 5.2 |
| | N | 1.8 | 0.9 | 1.4 | 1.6 | 1.3 | 1.0 |
| | S | 0.8 | 0.5 | 1.3 | 0.6 | 6.4 | 0.9 |
| | O | 9.7 | 17.3 | 8.4 | 5.7 | 10.7 | 18.5 |

Figure 1. Comparison of THF-insoluble residue concentration from reaction conducted at 450 °C, under 3.5 Mpa N₂, 60 min.

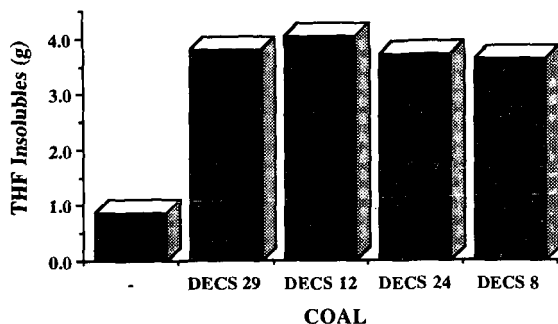


Figure 2. Comparison of THF-insoluble residue concentration from reaction conducted at 450 °C, under atmospheric N₂ environment, 120 min.

Table 3. Results of Simulated Delayed Coking of Vacuum Resid and Selected Coals at 450 °C for 2 hours, under atmospheric N₂.

| Feed | | Conversion (wt%, daf) | Liquid Product Distribution (wt%, daf) | | |
|-------|---------------|--------------------------|--|------|---------|
| Resid | Coal | | Oils | Asph | Preasph |
| VR1 | - | 80.6 | 4.8 | 2.1 | 0.7 |
| VR1 | Upper Banner | -37.5 | 10.4 | 5.4 | 2.9 |
| VR1 | Pittsburgh #8 | -39.0 | 6.6 | 5.3 | 2.8 |
| VR1 | Illinois #6 | -36.6 | 11.6 | 4.9 | 2.5 |
| VR1 | Wyodak | -27.4 | 8.0 | 7.2 | 2.8 |

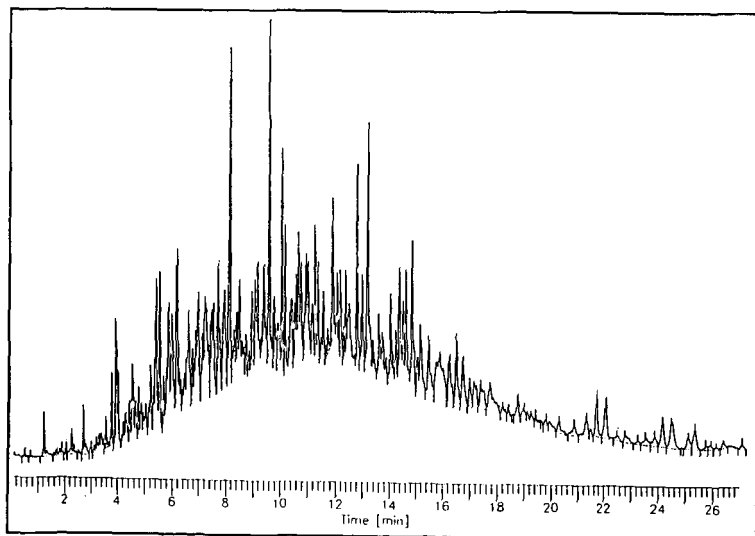


Figure 3. Chromatogram of n-Hexane Solubles from Co-coking Upper Banner with VR1, 120 min, atmospheric N₂ environment.